CONTRIBUTIONS

TO THE

CHEMISTRY OF THE URINE.

ON THE VARIATIONS IN THE

ALKALINE AND EARTHY PHOSPHATES IN THE HEALTHY STATE,

AND ON

THE ALKALESCENCE OF THE URINE FROM FIXED ALKALIES.

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XV. *Contributions to the Chemistry of the Urine. On the Variations in the Alkaline and Earthy Phosphates in the Healthy State, and on the Alkalescence of the Urine from Fixed Alkalies. By* Henry Bence Jones, *M.A., Cantab., Fellow of the College of Physicians. Communicated by* S. Hunter Christie, *Esq., Sec. R.S.*

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On the Variations of the Earthy and Alkaline Phosphates in a healthy state of Urine.

HAVING observed the occurrence of a great excess of earthy phosphates in the urine in some cases of disease, and having made frequent examinations as to the quantity present on successive days, I found so great a discrepancy, that it became necessary before any further progress could be made to ascertain the variations in the amount of earthy phosphates in the urine of a healthy man, and, if possible, to trace the causes which determined the presence of an excess or deficiency of these salts in the urine. At the same time it was thought desirable to note the variations which the alkaline phosphates presented in the same water, and to see if they were influenced by the same, or by different causes.

A healthy man taking food twice daily, with moderate exercise for three hours, was the subject of the following experiments. The method followed was to take the specific gravity of the urine, if ever it was not strongly acid adding a drop or two of hydrochloric acid. Then from a weighed quantity, usually about 1000 grains, to precipitate the earthy phosphates by means of pure ammonia, to filter, wash with ammoniacal water, and heat them to redness, adding at last a drop or two of nitric acid. Thus the earthy phosphates were determined.

The alkaline phosphates were estimated by taking usually about 500 grains of urine, adding an excess of chloride of calcium and then pure ammonia; by this means all phosphoric acid was precipitated as phosphate of lime; this was filtered, well-washed, and heated to redness with nitric acid; by deducting the previously determined earthy phosphates, the difference was considered as alkaline phosphate*.

Though neither the calculation nor the method were perfectly accurate, yet they answered well for the purposes of comparison; and in disease the short delay before a result was arrived at which might determine the diagnosis, and sometimes the treat-

* The formation of a small quantity of carbonate of ammonia and the precipitation of some sulphate of lime, which even long washing cannot entirely remove, make the result too high. The equivalent of lime being less than that of soda tends to reduce the error. It must be remembered that the phosphoric acid is precipitated in combination with three equivalents of lime.

ment, was a matter of considerable importance; a few hours being usually all that were required to tell in what excess or deficiency the phosphates might be present.

I. (1.) Breakfast on bread and meat with coffee at 9½ o'clock. Dinner at 6: meat, potatoes, and little bread.

		Earthy phosphates.	Spec. gr.	Alkaline phosphates.
Water passed	6 o'clock, evening	·32 per 1000 urine	1022·8	6·50 per 1000 urine.
	10 o'clock, evening	·97	1027·3	5·45
	6 o'clock, morning	·81	1017·4	4·01
(2.) Food as before. More exercise. Dinner at 7.				
	7 o'clock, evening	·37	1027·2	7·26
	11 o'clock, evening	1·22	1029·9	6·06
	5 o'clock, morning	1·41	1025·5	3·64
(3.) Food as before. Still more exercise.				
	7 o'clock, evening	·75	1028·0	8·10
	12 at night	1·29	1025·5	6·67
(4.) Food as before. Exercise very great excess.				
	7 o'clock, evening	·21	1028·2	8·22
	1 at night	1·85	1034·3	5·94
(5.) Food as before. Exercise much less.				
	7 o'clock, evening	·35	1029·3	7·75
	1 at night	1·91	1033·2	4·72

Average mean of five days.	Long after food, and soon after exercise.	Spec. gr.	Soon after food with perfect rest.	Spec. gr.
Earthy phosphates	·40 per 1000 urine	1027·9	1·45 per 1000 urine	1030·0
Alkaline phosphates	7·56	1027·9	5·77	1030·0

From this five days' experiment, it appears that the earthy phosphates are greatly increased in the water secreted soon after food; the quantity varying after dinner from 1·91 per 1000 urine, specific gravity 1033·2, to ·97 per 1000 urine, specific gravity 1027·3; the mean of all the experiments being 1·45 per 1000 urine, specific gravity 1030·0.

The earthy phosphates are far less in the water secreted a long time after food; the quantity varying from ·21 per 1000 urine, specific gravity 1028·2, to ·75 per 1000 urine, specific gravity 1028·0; the mean of all the experiments being ·40 per 1000 urine, specific gravity 1027·9.

The alkaline phosphates are in excess in the water secreted a long time after food and soon after exercise; the quantity varying from 8·10 per 1000 urine, specific gravity 1028·0, to 6·50 per 1000 urine, specific gravity 1022·8; the mean of all the experiments being 7·56 per 1000 urine, specific gravity 1027·9.

The alkaline phosphates are far less in the water secreted soon after food; the quantity varying from 6·67 per 1000 urine, specific gravity 1025·5, to 4·72 per 1000 urine, specific gravity 1033·2; the mean of all the experiments being 5·77 per 1000 urine, specific gravity 1030·0.

(6.) A child twenty months old, fed on bread with some meat and milk, gave in the water passed during the day,—

Earthy phosphates.	Spec. gr.	Alkaline phosphates.
·32 per 1000 urine.	1012·2	4·00 per 1000 urine.

(7.) On the same food.

Earthy phosphates.	Spec. gr.	Alkaline phosphates.
·33 per 100 urine.	1017·4	4·60 per 1000 urine.

II. I next endeavoured to ascertain on what the variations depended, and first with regard to food. For three consecutive days bread alone was taken with water, tea and wine, at the same hours as in the previous experiments.

(8.) The first day brown bread only.

	Earthy phosphates.	Spec. gr.	Alkaline phosphates.
5½ o'clock, evening	·27 per 1000 urine	1025·7	7·89 per 1000 urine
11 at night.	1·37	1030·0	6·39

(9.) The second day no analysis was made. The third day white bread only.

	Earthy phosphates.	Spec. gr.	Alkaline phosphates.
6 o'clock, evening	·37 per 1000 urine	1024·7	8·19 per 1000 urine
11 o'clock, evening	1·86	1032·1	5·56

(10.) Meat only was taken for three days with water, wine, and tea. First day exercise very little.

	Earthy phosphates.	Spec. gr.	Alkaline phosphates.
6 o'clock, evening	·42 per 1000 urine	1024·3	4·04 per 1000 urine
11 o'clock, evening	1·11	1021·9	4·21

(11.) The second day no analysis was made. The third day exercise rather more.

	Earthy phosphates.	Spec. gr.	Alkaline phosphates.
6 o'clock, evening	·48 per 1000 urine	1024·7	5·06 per 1000 urine
11 o'clock, evening	·81	1024·8	4·31

(12.) Meat only for dinner with distilled water, and tea with distilled water.

	Earthy phosphates.	Spec. gr.
5½ o'clock, evening	·33 per 1000 urine	1025·7
9½ o'clock, evening	·67	1026·5

From the comparison of these numbers with the previously given average, it appears that the earthy phosphates are not materially influenced by a diet of meat or diet of bread; that they are in excess after either is taken; and that even when animal food and distilled water alone were taken there was after food a decided increase, though the quantity was considerably below the average.

That the alkaline phosphates were in excess when bread alone was taken for food; and when meat alone was taken there was a considerable falling off in the amount excreted.

The next point was the effect of exercise.

(13.) Nothing was taken from dinner on the previous day to dinner this day; both meals consisted of mixed diet of meat, bread, and potatoes. The exercise was moderate, between three and six o'clock.

	Earthy phosphates.	Spec. gr.	Alkaline phosphates.
$12\frac{1}{2}$ o'clock	·45 per 1000 urine	1025·1	2·95 per 1000 urine
3 o'clock	·48	1026·0	2·92
6 o'clock		1027·1	total phos. per 1000 urine 4·77
$10\frac{1}{2}$ at night	1·02	1027·6	3·99

(14.) Nothing was taken since dinner on the previous day until dinner at six; mixed diet with more bread. Exercise also greater between 3 and $5\frac{1}{2}$ o'clock.

	Earthy phosphates.	Spec. gr.	Alkaline phosphates.
3 o'clock	·36 per 1000 urine	1025·4	5·69
6 o'clock		1027·1	total phos. per 1000 urine 7·78
$10\frac{1}{2}$ at night	1·37	1032·5	5·50

(15.) Nothing was taken since dinner on the previous day, which consisted of meat only, with distilled water and wine. Very strong exercise was taken between 3 and $5\frac{1}{2}$, the pulse always above 100.

	Earthy phosphates.	Spec. gr.	Alkaline phosphates.
$11\frac{1}{2}$ o'clock	·52 per 1000 urine	1022·9	3·04
3 o'clock	·36	1026·9	4·36
$5\frac{1}{2}$ o'clock		1028·9	total phos. per 1000 urine 6·81

In these experiments, the water, which was secreted longest after food, was not in sufficient quantity to admit of the determination of the earthy as well as alkaline phosphates. In all the experiments which were previously made, the exercise was always most between 3 and 6 o'clock, and yet at this time the earthy phosphates were always present in smallest quantity; so that the quantity of earthy phosphates does not appear to be quickly influenced by exercise.

The total quantity of phosphates which was found in the water secreted longest after food, and during strong exercise, was about one-third more than the total quantity previously present. This considerable increase so long after food, leads to the conclusion that the amount of alkaline phosphates is influenced by exercise, though, as appears from the previous experiments, not to the same extent as by the kind of food which is taken.

III. I pass now to the influence of different medicinal substances on the amount of earthy phosphates excreted.

(16.) Breakfast as before, at 9 o'clock. 15 grains of chloride of calcium taken in about an ounce of distilled water at 3 o'clock.

	Earthy phosphates.	Spec. gr.
3 o'clock	·30 per 1000 urine	1024·6
$5\frac{1}{2}$ o'clock	·22	1016·4

(17.) Experiment repeated.

	Earthy phosphates.	Spec. gr.
3 o'clock	·67 per 1000 urine	1024·4
5½ o'clock	·52	1020·8

(18.) Breakfast, bread only. 22 grains of chloride of calcium taken at ¼ to 1 o'clock.

	Earthy phosphates.	Spec. gr.
¼ to 1 o'clock	1·18 per 1000 urine	1028·6
3 o'clock	1·08	1025·2

(19.) Breakfast, bread and meat. 35 grs. of chloride of calcium in 1½ ounce of water at ¼ to 1.

	Earthy phosphates.	Spec. gr.
¼ to 1 o'clock	1·23 per 1000 urine	1026·8
3 o'clock	1·26	1023·8
5½ o'clock	1·08	1022·3
10¼ at night	1·82	1030·1

(20.) Breakfast, bread and meat. No chloride of calcium taken. Dinner as before at 6, chiefly meat.

	Earthy phosphates.	Spec. gr.
3 o'clock	·60 per 1000 urine	1027·4
6 o'clock	·36	1027·0
11 at night	·97	1032·7

From these experiments 15 grs. of chloride of calcium in an ounce of water produced no, or very little, effect in two hours and a half; 22 grs. in rather more water produced an increase in two hours and a quarter; 30 grains produced a still more marked increase in the same time, and the effect continued to be perceptible for at least ten hours.

(21.) Breakfast as before, with rather more meat. 30 grains of dry sulphate of magnesia were taken at 1 o'clock in about an ounce and a half of distilled water.

	Earthy phosphates.	Spec. gr.
1 o'clock water	·82 per 1000 urine	1026·6
3 o'clock water	·27	1026·0
5¼ o'clock water	·36 -	1025·8

(22.) Breakfast at 9 as formerly. 40 grains of dry sulphate of magnesia taken in about two ounces and a half of water at a ¼ to 1 o'clock.

	Earthy phosphates.	Spec. gr.
¼ to 1 o'clock water	·88 per 1000 urine	1029·3
3 o'clock water	·74	1031·0
5½ o'clock water	·90	1029·3
9½ o'clock water	1·64	1032·3

(23.) A patient of Dr. Seymour's in St. George's Hospital had taken senna with

about two drachms of sulphate of magnesia in the morning, which did not act on the bowels; at 12 beef-tea and bread.

	Earthy phosphates.	Spec. gr.
3 o'clock	2·99 per 1000 urine	1027·6

A second experiment with the same urine, at the same time, gave nearly the same result; the alkaline phosphates were only 1·45 per 1000 urine, specific gravity 1027·6.

(24.) Another patient of Dr. SEYMOUR's in St. George's Hospital, who had taken senna and salts in the morning, with beef-tea and arrow-root for dinner, gave

Earthy phosphates.	Spec. gr.
2·93 per 1000 urine	1026·2

The quantity of sulphuric acid present in this urine

=3·21 per 1000 urine, specific gravity 1026·2

The amount given by BECQUEREL is = ·95 1018·9

The quantity stated by BECQUEREL is however below the average.

From these experiments, 30 grains of dry sulphate of magnesia in an ounce and a half of water produced no, or very little, effect in two hours. In four hours and a quarter the effect was distinctly visible. 40 grains in two ounces and a half of water produced a visible effect in two hours and a quarter, and a still more marked effect in four hours and three quarters. The effect continued to be perceptible for $9\frac{3}{4}$ hours after the medicine was taken.

As compared with the previous experiments, though the quantity taken appears to have been more, the effects seem not to have been so strongly marked; but in fact less of the base was taken in the last than in the previous set of experiments, for

30 grains of chloride of calcium are equivalent to 15·1 grains of lime,

40 grains of sulphate of magnesia are equivalent to 13·6 grains of magnesia.

As sulphate of magnesia is one cause of increase in the amount of earthy phosphates precipitated by ammonia, and as this salt also interferes in analyses regarding the quantity of sulphuric acid which is thrown out of the system, any means of knowing when it has been given as a medicine may be valuable. Most frequently it is prescribed with infusion of senna, which communicates a greenish yellow colour to the urine. This colouring matter, whether it has passed through the system or not, I find has the property of becoming of a deep red on the addition of an excess of any alkali, though it is most bright with ammonia. The red colour disappears again on neutralizing the alkali by an acid. It has a strong affinity for phosphate of lime. If rhubarb is taken, a less bright colour is given by the same reagents. I have lately found that Sir E. HOME in some of his experiments on absorption used the reaction of potash on tincture of rhubarb because it is so remarkable*.

(25.) Breakfast as before. 45 grains of dry magnesia taken at 10 o'clock. It had no action at all on the bowels.

* Philosophical Transactions, 1808, p. 45. According to the researches of SCHLOSSBERGER, this reaction is caused by chrysophanic acid which exists in the rhubarb.—Annalen der Chemie, vol. l. p. 214.

	Earthy phosphates.	Spec. gr.
$11\frac{1}{4}$ o'clock, water acid	·90 per 1000 urine	1026·7
$\frac{1}{4}$ to 1 o'clock, water alkaline	·69	1027·8
3 o'clock, water alkaline	1·19	1029·6
$5\frac{1}{2}$ o'clock, water very acid	1·48	1028·0
10 o'clock, water very acid	2·69	1032·8

(26.) Breakfast as before. 30·8 grains of magnesia taken at $\frac{1}{4}$ to 1. It did not act on the bowels.

	Earthy phosphates.	Spec. gr.
$\frac{1}{4}$ to 1 o'clock, water acid	1·79 per 1000 urine	1030·4
3 o'clock, water acid	1·19	1032·2
4, $5\frac{1}{2}$ o'clock, both acid	1·69	1032·3
$9\frac{1}{2}$ o'clock, water very acid	2·44	1034·5

(27.) Breakfast as before. No magnesia taken.

	Earthy phosphates.	Spec. gr.
3 o'clock	1·00 per 1000 urine	1030·3
6 o'clock	·59	1031·4
$9\frac{1}{2}$ o'clock	1·39	1031·6

Hence 45 grains of magnesia produced no increase in the phosphates in two hours and three quarters; in five hours there was a marked increase; in seven and a half hours there was a still further increase, which was very marked at the end of twelve hours, and from the large quantity of earthy phosphates present the following morning, perhaps the magnesia had not ceased to act in twenty-four hours.

30·8 grains of magnesia produced no evident increase in two hours and a quarter; in four hours and three quarters the increase was marked, and after eight hours and three quarters it was quite perceptible. From the analysis of the urine after twenty-six hours, it seems probable that the magnesia had not then ceased to influence the amount of earthy phosphates.

(28.) Water of the same child as (6.) and (7.) 15·4 grains of magnesia taken about $7\frac{1}{2}$ o'clock. Did not operate until after last water was passed. Food as before.

	Earthy phosphates.	Spec. gr.
11 to 1 o'clock, water alkaline	·62 per 1000 urine	1025·3
3 to 5 o'clock, water acid	1·57 per 1000 urine	1027·7

(29.) Same child. Food as before. No magnesia.

	Earthy phosphates.	Spec. gr.
2 to 5 o'clock, water acid	·36 per 1000 urine	1018·5

(30.) Same child. 19·3 grains of magnesia at 8 o'clock. Medicine acted about three o'clock.

	Earthy phosphates.	Spec. gr.
11 to 1 o'clock, water neutral	·45 per 1000 urine	1014·4
3 to 5 o'clock, water acid	·80	1017·1

The conclusions from these experiments are—

I. As regards variation in the phosphates.

The earthy phosphates soon after food were found to vary from 1·91 per 1000 urine, specific gravity 1033·2, to ·97 per 1000 urine, specific gravity 1027·3.

Long after food they vary from ·21 per 1000 urine, specific gravity 1028·2 to ·75 per 1000 urine, specific gravity 1028·0.

The alkaline phosphates long after food, and soon after exercise, vary from 8·10 per 1000 urine, specific gravity 1028·0, to 6·50 per 1000 urine, specific gravity 1022·8.

Long after food the quantity varies from 6·67 per 1000 urine, specific gravity 1025·5, to 4·72 per 1000 urine, specific gravity 1033·2.

II. As to the causes of the variation.

(*a.*) As regards food.

The earthy phosphates were not materially influenced by a diet of meat or of bread. They were in excess after either was taken; but on distilled water and meat alone, the excess was considerably below the average.

A long time after food the earthy phosphates were greatly diminished.

The alkaline phosphates were present in greatest quantity when bread alone was taken for food; when meat alone was taken, the deficiency was more marked than the excess with bread alone was. There was the most marked difference when the bread diet was compared with the meat diet.

(*b.*) As regards exercise.

Exercise produced no marked effect on the earthy phosphates.

On the alkaline phosphates exercise caused an increase of nearly one-third the amount previously excreted. This difference is not so great as that between bread and meat diets; so that probably though exercise has some influence, the kind of diet has a greater influence.

III. As to the effect of medical substances on the earthy phosphates.

(*a.*) As regards chloride of calcium.

15 grains of chloride of calcium produced no, or very little, effect in two hours and a half.

22 grains in rather more water produced a very decided increase in two hours and a quarter.

30 grains produced a still more marked increase in the same time, and the effect continued to be perceptible for ten hours.

(*b.*) As regards sulphate of magnesia.

30 grains of sulphate of magnesia in $1\frac{1}{2}$℥ water produced no, or very little, effect in two hours; in four hours and a quarter an increase was distinctly visible.

40 grains in $2\frac{1}{4}$℥ of water produced a very slight effect in two hours and a quarter; in $4\frac{3}{4}$ hours an increase was very distinct, and continued to be perceptible for nine hours.

(*c.*) As regards calcined magnesia.

45 grains of magnesia produced no effect in two hours and three quarters; in five hours there was a marked increase; in seven hours and a half a still greater increase, which was very marked at the end of twelve hours, and possibly continued for twenty-seven hours to influence the amount of earthy phosphates.

30·8 grains of magnesia produced no increase in two hours and a quarter; in four hours and three quarters the increase was very evident; and after eight hours and three-quarters it was still very marked; and after even twenty-six hours it still increased the amount of earthy phosphates in the urine.

These last experiments give the explanation of the rapid increase of phosphatic calculi, and of the enormous quantities of earthy matter discharged, when magnesia or lime-water have been taken in calculous affections. They show that these substances, having probably combined with different acids, pass off by the urine, and when this latter is alkaline react on the phosphate of soda, and thus increase considerably the amount of earthy phosphates in the deposit.

The result of these experiments is, that the amount of earthy phosphates precipitable by ammonia, depends chiefly on the amount of earthy matter taken into the body; and that the amount of alkaline phosphates is also most chiefly influenced by diet; yet that there is an additional cause constantly acting in the state of health, namely the production of phosphoric acid by the changes in the tissues of the body. And as in disease some of these tissues may be more particularly engaged, so then may the amount of alkaline phosphates point out the character, and declare the nature of the structure which is the seat of the affection.

On Alkalescence of the Urine from fixed Alkali.

The cases in which the urine is alkaline may be divided into two classes. In the one the alkalescence arises from volatile alkali, and in the other from fixed alkali. In the first it is caused by carbonate of ammonia, and in the second by carbonate of soda, or potash, or alkaline phosphate of soda. Decomposition of urea is the origin of the one, and disordered secretion of the other.

Whenever alkalescence arises, the earthy phosphates, whatever their quantity, are generally precipitated; and hence the expression phosphatic diathesis, a term which makes no distinction between the different kinds of alkalescence, nor between cases in which the earthy phosphates, sometimes far below their average quantity, simply appear in consequence of their insolubility in alkaline fluids, and cases in which a vast excess of earthy or alkaline phosphates is being excreted.

The object of the present paper is to point out the fact and the value of the distinction between the different kinds of alkalescence.

M. Pelouze has shown how rapidly decomposing mucus effects the conversion of urea into carbonate of ammonia. Irritation of the mucous membrane may give rise to mucus which produces this change, and in consequence the blue colour will be restored to reddened litmus paper if dipped into urine containing such mucus; or if

blue paper be used, this, whilst wet, will retain its colour; but if the test-paper be left to dry in either case it will be found that a change takes place. From the reddened litmus paper first used the blue colour will disappear, whilst the blue paper, when quite dry, will become red in consequence of a slight decomposition of the ammoniacal salt. This decomposition I have elsewhere shown to be the result of the evaporation of all ammoniacal solutions, and thus a ready and easy way is afforded of determining in any case of the alkalescence of the urine, whether it is caused by some ammoniacal salt, or whether it results from the presence of some fixed alkali*.

It not unfrequently happens that alkalescence is caused by fixed alkaline salts in those who, though not ill, yet suffer from indigestion whilst leading sedentary lives. I have more especially observed it where the octahedral crystals, usually supposed to be oxalate of lime, have been present. After a breakfast consisting chiefly of bread, in an hour and a half the water passed may be found healthily acid to test-paper, but that which is next passed, that is, from two to four hours after breakfast, will have an alkaline reaction. Frequently blue test-paper will be found, when dry, to undergo no change from the action of such urine. It will remain of nearly as deep a blue as before when the fluid has perfectly evaporated. This urine when passed will, though alkaline, often be perfectly clear, and if it be heated a granular precipitate will fall, the fluid becoming turbid from the deposit of earthy phosphates, which dissolve in dilute hydrochloric acid, usually without any effervescence.

Such a precipitation by heat takes place when the urine is not even neutral. It may be slightly acid. When boiled a precipitate falls, and if the fluid is then tested it is found to be more acid than before. If such a deposit from acid urine is left to become cold, the earthy phosphates are found to be partially, and sometimes even entirely redissolved, being again precipitable by boiling, and again partially or entirely dissolving on cooling.

If such urine as I have mentioned is passed alkaline and thick from deposit, it will be found, if immediately examined by the microscope, to be entirely granular (Plate V. fig. 2), the supposed form of phosphate of lime. Dilute hydrochloric acid, if added occasionally causes an effervescence, which in some cases arises from some alkaline carbonate in solution.

If the alkalescent or neutral urine is left for some hours, the surface becomes covered with an iridescent pellicle (fig. 1). This examined with the microscope contained here and there a long prismatic crystal, but the pellicle itself consisted of plates covered with spots of amorphous deposit. Some of these were triangular, some quadrilateral, some with regular and others with a ragged margin. The iridescence depended on these plates, which probably consist of phosphate of lime, as in some cases not a single prismatic crystal has been visible.

In some who suffer from indigestion the deposit of amorphous phosphate is con-

* This method, however, I have found to fail when much urate of ammonia and only a small quantity of fixed alkali chanced to be present.

stantly seen about three hours after breakfast, and very rarely at other times. In others the alkalescence of the urine is frequently observed, but the deposit is rare; whilst in others the deposit by heat from acid urine is very frequently to be found; and alkalescence is seldom to be detected by test-paper in the water secreted from two to four hours after food, and these three states often alternately occur in the same case.

Dr. ANDREWS of Belfast stated to me, that having observed a case otherwise in perfect health, in which the urine was almost invariably alkaline about two hours after breakfast, so much so as frequently to be loaded with a deposition of phosphates whilst still in the bladder, he was led to observe the urine of about fifteen students in good health immediately after it was voided about noon. He found it to be alkaline in about two-thirds of the cases. Whether this tendency to alkalescent urine may, as Dr. ANDREWS thinks, be connected with the immunity enjoyed by the inhabitants of his district from calculous affections, or whether alkalescence at this period of the day is far more general everywhere than has been supposed, future observations must determine.

At the present time I know five physicians in whom the above phenomena at this period of the day are more or less frequently visible in a greater or lesser degree; and in London this alkalescence will be found in those who are considered generally healthy much oftener than is imagined.

Supposing that acid phosphate of soda was the cause of the acid reaction of healthy urine, it was thought that some explanation of the deposit on boiling might be gained by observing the behaviour of phosphate of lime and phosphate of magnesia with phosphate and biphosphate of soda. Pure solutions of these salts and of chloride of calcium, and sulphate of magnesia were used, and the following results obtained. The deposits were examined with a magnifying power of 320 times.

Chloride of calcium gave no immediate precipitate with a strong solution of acid phosphate of soda. If left to stand many hours, a crystalline precipitate formed (fig. 3). When boiled no cloudiness was observed, if the quantity of phosphate of lime present was small; but if much was in solution, a crystalline precipitate fell on boiling; and when cold, if filtered and again boiled, a very small crystalline precipitate was occasioned, which did not entirely redissolve on cooling.

When a solution of biphosphate of soda is mixed with chloride of calcium, an immediate precipitate is caused by a drop or two of any alkali, and this is crystalline (fig. 3), or granular (fig. 2), or these mixed according to the quantity of alkali added, that is, according as much or little of the acidity of the solution is removed.

If this precipitate was separated by filtration and the clear liquid boiled, a deposit fell which was at first gelatinous (fig. 2), the fluid becoming more acid to test-paper. The precipitate, if the solution was very acid, changed into the crystalline form (fig. 3), and partly dissolved on cooling.

If chloride of calcium was added to common phosphate of soda, a plentiful granular

precipitate fell (fig. 2). This remained granular or changed into the crystalline form (fig. 3), according as the phosphate of soda was or was not in excess. If the chloride of calcium was added in excess, the fluid became acid to test-paper; the precipitate was at first gelatinous, but changed after some hours into crystalline, the fluid becoming less acid after some time. If phosphate of soda was in excess, the precipitate remained of a mixed granular and crystalline appearance, containing some crystals but more granular phosphate of lime (fig. 4).

If common phosphate of soda was poured drop by drop into chloride of calcium, a precipitate fell, which was at first gelatinous (fig. 2), the fluid becoming strongly acid to test-paper; if left to stand, the precipitate became crystalline (fig. 3), and at length lost some or all its acid reaction, which it reacquired again on boiling.

If common phosphate of soda was dropped into solution of nitrate of lime in excess, the result was the same gelatinous granular precipitate first forming, the same acid reaction, and the same change into the crystalline form on standing.

If any of these precipitates were separated by filtration, and the clear liquid boiled, a further slight precipitation occurred, which was granular (fig. 2). If the phosphate of soda was not in excess, the boiling caused an increase in the acid reaction of the liquid. The precipitate which falls when chloride of calcium is added to phosphate of soda, completely dissolves in solution of biphosphate of soda. Such a solution, if heated, gave a plentiful precipitate when boiled; this was granular, and partly dissolved on cooling; but if a great excess of biphosphate of soda was added, the precipitate was much less, and crystalline; and if filtered, but little precipitate again fell on boiling.

If sulphate of magnesia was added to a solution of biphosphate of soda, no precipitate fell; nor on boiling did any change occur. If but little alkali was added, no precipitation occurred on boiling; if rather more, a small, highly crystalline precipitate fell (fig. 5); if still more, heat threw down a plentiful gelatinous granular mass (fig. 2), which most rapidly dissolved on cooling.

If sulphate of magnesia was added to common phosphate of soda, little or no precipitate occurred, but if boiled a gelatinous precipitate fell; this dissolved as the fluid cooled. Under the microscope it was seen to be amorphous (fig. 2). If it was in such excess as not entirely to redissolve on cooling, a few drops of biphosphate immediately made the liquid clear. This, if boiled, gave a plentiful precipitate, and more quickly dissolved on cooling than before. If the liquid was very acid from biphosphate of soda, a slight crystalline precipitate fell, consisting of minute rhombic crystals, similar to those which were seen in the experiment with biphosphate of soda (fig. 5).

If a solution of phosphate of soda was dropped into an excess of sulphate of magnesia, after long standing a crystallization of small needles took place (fig. 6), but the fluid did not become acid to test-paper: nor if dropped into an excess of solution of chloride of magnesium was an acid reaction perceptible.

If to perfectly healthy and strongly acid urine a drop or two of a solution of chloride of calcium is added, no precipitate falls. If the acidity is lessened by any alkali, on boiling a granular precipitate is occasioned. This, when the urine is still acid, is partly or entirely redissolved on cooling; or if alkaline, immediately dissolves in dilute hydrochloric acid without any trace of effervescence.

Between three and five hours after food, at which time the earthy phosphates are always in excess, if healthy acid urine which gives no deposit on boiling has some of its acidity removed by fixed alkalies, or alkaline phosphate, a deposit takes place on boiling, and this is always granular, the fluid becoming more acid than before.

If to such alkaline urine as is passed thick from earthy phosphate a little biphosphate of soda is added, the phosphate redissolves; and if the biphosphate is not added in excess the earthy phosphates can be precipitated by heat, the reaction becoming more acid; but if an excess be added, the fluid remains perfectly clear on boiling.

There is then the closest coincidence between the deposits of earthy phosphates in some states of the urine, and their deposit from solutions of the phosphates of soda; and the same method which is followed for obtaining a precipitate of earthy phosphates dissolved in biphosphate of soda, will give a precipitate from healthy acid urine, and that which hinders precipitation in the one has the same effect on the other.

The deposit of phosphate of magnesia by boiling was supposed by M. Riffault to depend on the formation of a more basic phosphate of magnesia. The same explanation is still more probably the truth regarding the precipitation of the phosphate of lime by boiling, whether from solutions of phosphates of soda or from the urine.

The formation of crystalline earthy phosphates when great excess of earthy phosphate was present while at the same time the biphosphate of soda made the liquid very acid, gives the explanation why crystalline phosphate of lime is so seldom seen in the urine. Still it may occasionally be met with. Crystalline phosphate of magnesia, from its greater solubility, can scarcely appear. The amorphous deposit of phosphate of magnesia when urine is boiled may perhaps be recognised by its far greater solubility than the phosphate of lime as the fluid cools.

In the state of health acid phosphate of soda, mixed probably with common phosphate of soda, holds the earthy phosphates in solution. No precipitate is occasioned by chloride of calcium. If, after the water is passed or before from medicines, or particular food, or state of body, some of the acid phosphate is converted into common phosphate, a precipitate takes place on boiling the acid urine. If this very rapidly dissolves before the fluid is cold, the precipitate contains most probably phosphate of magnesia; if very slowly, it is more likely to be phosphate of lime. If the urine be neutral to test-paper, that is, contains still less biphosphate of soda (the common phosphate being decidedly alkaline to test-paper), then the precipitation

is more marked and the re-solution on cooling very much less. If the urine be alkaline, containing only common phosphate, this may be passed clear, and still may contain some phosphate of magnesia and a little phosphate of lime, these being somewhat soluble in common phosphate of soda, and these will be precipitated on boiling.

If the phosphate of lime is from any cause in great excess, it may be deposited as a granular deposit, and never in the crystalline form, unless it be in so great an excess that it is deposited from urine containing very much biphosphate of soda.

The occurrence of the alkaline condition at the particular period of the day which has been observed is well worthy of attention. The whole truth cannot be arrived at without a very lengthened inquiry into the variations in the amount of acids excreted by the kidneys, but partly at least it must depend on the food which has been taken in the morning, that is on the passage of alkaline phosphates, or carbonates, or salts of the vegetable acids through the system. Recent analyses of the ashes of seeds, flesh and blood, do not show any trace of alkaline carbonates, but as these cannot be heated to a red heat with common alkaline phosphates without the loss of carbonic acid, it will be seen how difficult it is to arrive at certainty on this point.

The conclusions from these observations are—

1. That there exist two kinds of alkalescence of the urine; the one long known as ammoniacal, the other not distinctly recognised, arising from fixed alkali. This last appears most frequently in water secreted from two to four hours after breakfast in persons suffering only from indigestion.

2. Water made at this period may be thick when passed from amorphous sediment, or it may be alkaline to test-paper, and still clear; or it may be free from deposit and slightly acid. If either of these last be heated, an amorphous precipitate may fall, which is soluble in dilute hydrochloric acid, or in solution of biphosphate of soda.

3. Healthy urine may at any time be made to give a precipitate of earthy phosphates by heat, even though it be acid, by having a little of its acid reaction removed by any alkali, or by common phosphate of soda, the fluid becoming more acid when boiled.

4. The solution of earthy phosphates in biphosphate of soda, gives also a precipitate on boiling if some of its acid reaction is removed by any alkali. The fluid when boiled becomes more acid to test-paper, indicating the formation of a more basic earthy phosphate.

5. A precisely similar result is obtained when common phosphate of soda, phosphate of lime, and a little biphosphate of soda exist in solution together; and by varying the quantities of each of these substances, the various phenomena which the urine occasionally presents may be produced at will.

6. The time at which the alkalescence of the urine from fixed alkali generally occurs, indicates the existence of some alkaline phosphate or of some carbonated alkali in the food*.

7. The result as regards diagnosis may be thus arranged :—

Alkalescence of the urine from local causes.	Alkalescence from general causes.
Blue paper made markedly red on drying.	Blue litmus paper not made red on drying.
Alkalescence constantly present.	Alkalescence variable, usually soon after food.
Always contains mucus in excess.	Rarely contains mucus in excess.
Prismatic crystals always to be found by microscope.	When first passed generally contains only granular deposit.

PLATE V.

Fig. 1. Iridescent pellicles on some alkaline urine.

Fig. 2. Amorphous deposit in alkaline urine.
Deposit on boiling phosphate of soda with chloride of calcium, or with sulphate of magnesia.

Fig. 3. Chloride of calcium with acid phosphate of soda, or with common phosphate of soda ; after long standing.

Fig. 4. Phosphate of soda with little chloride of calcium.
Bone-earth phosphate.

Fig. 5. On boiling phosphate of soda with sulphate of magnesia and little biphosphate of soda.

Fig. 6. Phosphate of soda with sulphate of magnesia; after long standing.

Appendix.

Later experiments have shown that the alkalescence from fixed alkali does not depend on the nature of the food. For example, with a diet of animal food and distilled water, the urine in four hours has been observed to be alkaline. Rather longer after dinner it has also been found to be alkaline. Usually however, after a late dinner, even if the water is secreted alkaline, it becomes mixed in the bladder during sleep with acid water which is afterwards secreted and thus the alkalescence escapes notice.

It seems highly probable that the quantity of acid poured out into the stomach sets free alkali sufficient in some cases to make the urine alkaline; and from facts which have been stated to me, it seems even possible that the same effect on the water may sometimes be produced by the separation of acid by the skin.

* See Appendix.

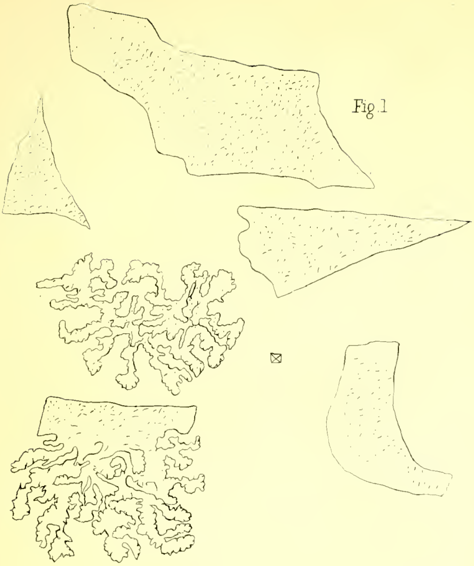

Fig. 1

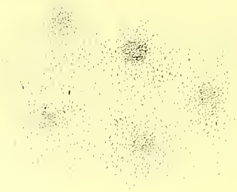

Fig. 2

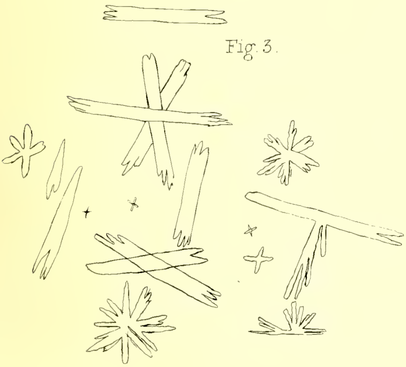

Fig. 3.

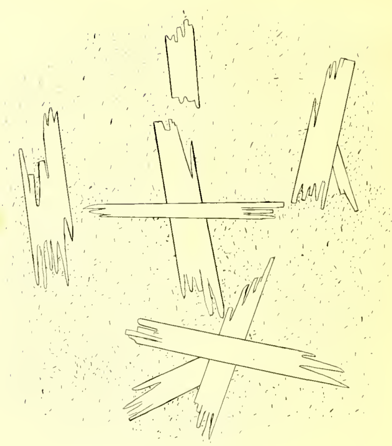

Fig. 4.

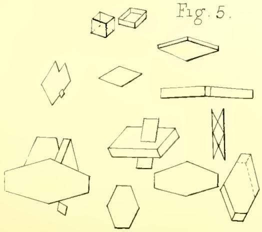

Fig. 5.

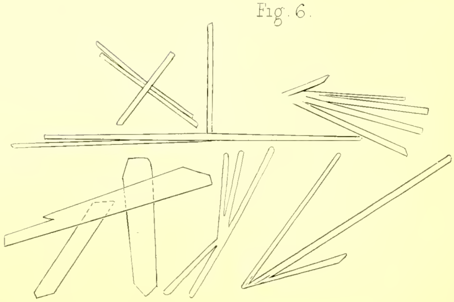

Fig. 6.

J. Basire, lith.